



Insight into hydroxyl groups in anchoring Ir single-atoms on vacancy-deficient rutile TiO₂ supports for selective catalytic oxidation of ammonia

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ABSTRACT

High-performance catalysts are extremely required for controlling NH₃ emission via selective catalytic oxidation (SCO), and the anchoring structural feature of active sites is a key prerequisite for developing them. This study confirms the importance of hydroxyl groups on vacancy-deficient reducible oxides as active groups. On the one hand, spontaneous atomic dispersion of active metal Ir is promoted by the abundant terminal hydroxyl groups. On the other hand, Ir cations anchor on the TiO₂ surface through exchange with H⁺ in Ti-OH groups, and thus occupy the Brønsted acid sites. The adsorption strength of NH₃ is another key factor affecting the reaction rate-determining step, namely NH₃ dehydrogenation, which occurs at a faster rate in the coordinated L-NH₃ rather than the ionic B-NH₄⁺. Meanwhile, the coordinated L-NH₃ significantly avoids the competitive adsorption of water vapor in the NH₃-SCO reaction by reducing the number of hydrogen bonding. The TOF of preferred 0.8Ir/TiO₂ sample is significantly higher than 0.2Ir/TiO₂ sample, although Ir is almost always atomic dispersed. Finally, NH₃ conversion is 85% in a wet circumstance (5% H₂O) at 240 °C (GHSV = 85 000 h⁻¹), with a N₂ selectivity of up to 65% on 0.8Ir/TiO₂ sample.

1. Introduction

NH₃ selective catalytic reduction (NH₃-SCR) has become the most widely used technology to reduce the emission of nitrogen oxides (NO_x) from both coal-fired industries and diesel engines [1–3]. The increasingly stringent emission regulations require that the injection amount of reducing agent usually exceeds the theoretical chemistry stoichiometric ratio, resulting in a serious problem of NH₃ slip [4]. Gaseous NH₃ is considered to be an important precursor of particulate matter with average diameters smaller than 2.5 μm (PM_{2.5}), which contributes to the formation of haze and serious health issues [5,6]. In order to avoid potential harm to human health and the ecological environment, the allowable NH₃ slip concentration for the SCR system in industrial

industries such as coal-fired in China has been tentatively regulated to be less than 3 ppm [7].

Selective catalytic oxidation of NH₃ (hereafter referred to as NH₃-SCO) into N₂ using catalysts has been regarded as a particularly promising process of decreasing the NH₃ emissions [8]. Noble metal catalysts, especially Pt- and Ag- based nanomaterials, have been widely investigated due to their excellent NH₃ conversion activity at the temperatures below 300 °C [9]. However, the active site is usually metallic aggregate particles, which lead to extremely low utilization of noble metals [10–13]. Iridium (Ir) is another typical noble metal, as reported in our previous research, the atomically dispersed Ir/TiO₂ catalyst has a clear activity advantage in NH₃-SCO reaction based on the “electronic metal-support interaction” (EMSI) [14]. The construction of sufficient

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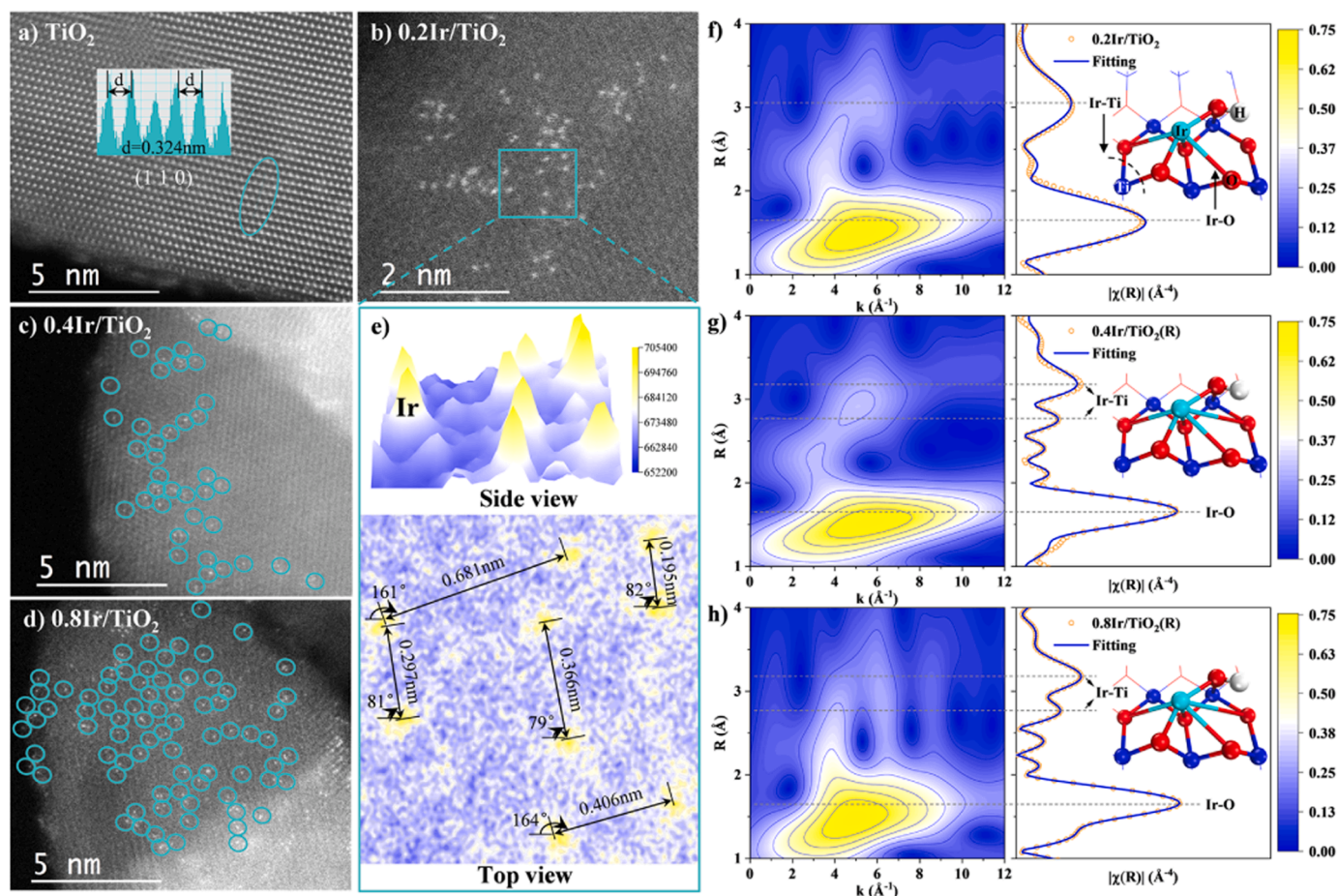


Fig. 1. HAADF-STEM images (a–e), WT-EXAFS contour plots and k^3 -weighted EXAFS spectra (f–h) of Ir/TiO₂ samples with different Ir loadings (0.2, 0.4 and 0.8 wt. %). (a) TiO₂, (b, e, f) 0.2Ir/TiO₂, (c, g) 0.4Ir/TiO₂, (d, h) 0.8Ir/TiO₂.

active sites by single-atom anchoring provides an effective pathway to improve the utilization of loaded metal [15], which has attracted extensive attention and discussion in recent years [16]. It is generally believed that stable metal single-atom need to be obtained by modifying and regulating the anchoring sites on appropriate supports, which are played by active groups [17].

Previous experiments and DFT calculations suggest that the defects are the direct mediators for the interaction between reducible oxides (TiO₂ and CeO₂, etc.) and active components [18–21]. Therefore, recent studies have focused on increasing the number of oxygen vacancies (labeled as O_v) in order to promote high dispersion of loaded metals and strengthen the reaction rate-determining step, i.e., NH₃ dehydrogenation. However, compared to anatase TiO₂ with abundant O_v [22], the capture of single-atom metals by O_v-deficient rutile TiO₂ is also very common [23,24]. Some other active groups on reducible oxides must be responsible for this metal atom capture. Typically, Kwak et al. reported the critical role of unsaturated penta-coordinated Al³⁺ (Al³⁺_{penta}) centers obtained by dehydration and dehydroxylation on Al₂O₃ in trapping Pt metal [25]. Dutov and Wang et al. respectively proposed that the hydroxyl (–OH) groups on SiO₂ and Al₂O₃ can maintain the stable dispersion of Ag [26,27]. However, the special role of these two sites in reducible oxide supports has not yet been elucidated. It is timely and necessary to reveal the anchoring mechanism of Ir species on TiO₂ for designing more effective Ir/TiO₂ catalysts or optimizing current catalysts using TiO₂ as the supports for NH₃–SCO reaction. Meanwhile, as a post catalyst for NH₃–SCR, NH₃–SCO materials need to meet high requirements for low-temperature activity and the resistance of flue gas components (e.g., water vapor) [28,29]. Hence, the reaction mechanism

of these active groups in the rate-determining step, namely NH₃ dehydrogenation, has become another prerequisite for developing high-performance catalysts.

In this work, Ir/TiO₂ samples with different Ir loadings are synthesized for correlating the O_v, unsaturated centers and –OH groups with Ir anchoring and calculating the binding energies of Ir at these sites. It is found that the relative amount of terminal –OH groups dominate the dispersion of Ir cations. While the type of acid sites on Ir/TiO₂ surface affects the NH₃ dehydrogenation rate and the competitive adsorption by water vapor. The conclusion improves the theoretical system of single-atom catalyst supported by reducible oxides and reveals the importance of hydroxyl groups as metal-support interactions media in catalytic reactions, which is significant for designing high-utilization catalysts.

2. Experimental

2.1. Catalyst preparation

Rutile TiO₂ was purchased from Aladdin chemicals. In detail, 6 g of TiO₂ was added in 250 mL of deionized water and the corresponding volume of iridium acetate solution (10 g·L⁻¹) was added. Typically, excess water was removed by a rotary evaporator at 60 °C under vacuum after stirring in water solvent for 1 h at about 25 °C. Then, the samples were dried 12 h at 110 °C and calcined at 400 °C in 20% O₂ + N₂ for 4 h (denoted as 0.2Ir/TiO₂, 0.4Ir/TiO₂, 0.8Ir/TiO₂ with Ir mass loading of 0.2, 0.4 and 0.8 wt.%, respectively). Finally, the samples were crushed and passed through a 40–60 mesh sieve before testing.

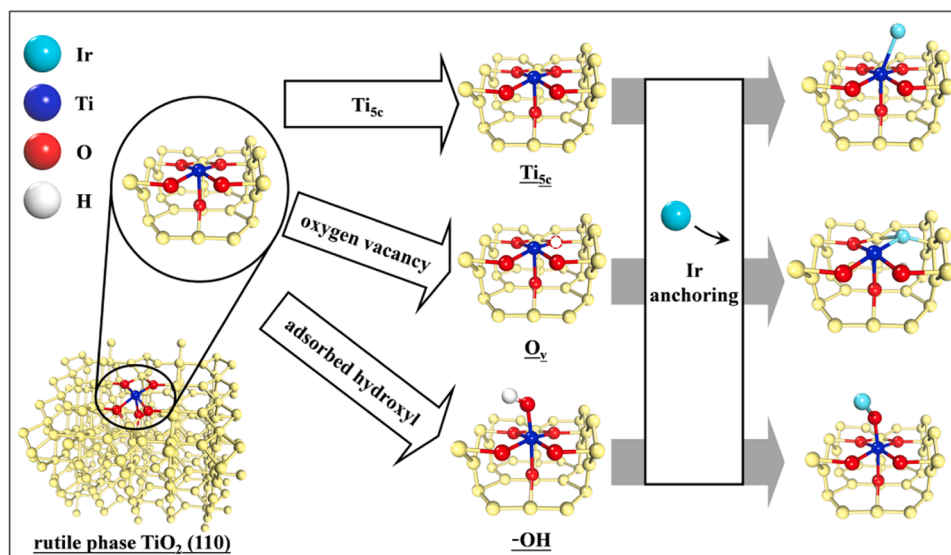


Fig. 2. A diagram showing three possible processes of Ir anchoring (Some of the periodic atoms in the model are replaced in yellow for emphasis).

2.2. Catalyst characterization

The samples were characterized by using various methods, including N_2 adsorption/desorption, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray Absorption Fine Structure (XAFS), X-ray photoelectron spectroscopy (XPS), Electron paramagnetic resonance (EPR), H_2 -temperature-programmed reduction (H_2 -TPR), NH_3 -temperature-programmed desorption (NH_3 -TPD), in situ diffuse reflectance infrared Fourier transformations spectroscopy (DRIFTS), and density functional theory (DFT) method. Bulk composition and the metal dispersion was measured by ICP-OES and H_2 chemisorption conducted on an Auto Chem II 2920. Detailed procedures are provided in [Supporting Information](#).

2.3. Catalytic evaluations

The activity measurements of NH_3 -SCO under atmospheric pressure were completed using a quartz tubular continuous flow reactor (inner diameter = 6 mm), with each sample weighing approximately 200 mg. The feed gas contained 400 ppm NH_3 , 10% O_2 , 5% H_2O (when used) and balanced N_2 . The total flow rate is 300 mL·min⁻¹ with a gas hourly space velocity (GHSV) of 85 000 h⁻¹. The gas concentrations of NH_3 , N_2O , NO , and NO_2 , were real time analyzed using an online FTIR spectrometer equipped with a DTGS detector. Turnover frequencies (TOFs) were obtained in a separate experiment where the conversion of NH_3 was kept below 30% by varying the GHSV (85 000–340 000 h⁻¹) with negligible heat and mass-transfer effects, and which are calculated using the Ir basis. The NH_3 conversion (X_{NH_3}), N_2 selectivity (S_{N_2}) and TOF were calculated as below:

$$X_{NH_3} = \left[1 - \frac{NH_3(out)}{NH_3(in)} \right] \times 100\% \quad (1)$$

$$S_{N_2} = \frac{[NH_3(in) - NH_3(out)] - 2 \times N_2O(out) - NO(out) - NO_2(out)}{[NH_3(in) - NH_3(out)]} \times 100\% \quad (2)$$

$$TOF = \frac{X_{NH_3} \times Q \times NH_3(in) / (60 \times V_m)}{m \times w \times D/M} \quad (3)$$

Where Q , V_m , m , w , D , M are total flow rate, molar volume of gas, catalyst quality, loading of Ir, dispersion of Ir, molar mass of Ir atom, respectively.

The catalysts were stabilized for 120 min at each temperature point, and the gas concentrations were recorded for the last 10 min and averaged.

3. Results and discussion

3.1. Dispersion and coordination state of Ir species

Aberration-corrected HAADF-STEM measurements were performed to investigate the Ir dispersion for Ir/TiO₂ catalysts with different loading. As shown in Fig. 1a, the lattice spacing of TiO₂ is 0.324 nm, corresponding to the (110) plane of its rutile phase (PDF No. 00-021-1276) [30,31]. According to the principle of Z-contrast imaging, the image intensity of an element is proportional to the square of its atomic number (Z) [32]. Therefore, the image intensity of Ir (Z = 77) atoms is higher than that of Ti (Z = 22) atoms. The isolated bright spots belonging to single-atom Ir₁ species can be clearly identified for all the Ir/TiO₂ samples [33], as marked by the blue circles (Fig. 1b–d). It should be noted that the distribution of single-atom Ir₁ is random on the surface of TiO₂ substrate for loaded Ir/TiO₂ samples, rather than embedded in the lattice. The randomness can be further analyzed in the selected-area intensity surface plot, and the distance and angle between two atoms vary greatly within the selected range (Fig. 1e). The failure to form ordered crystal structures is an important feature of atomic dispersion.

XAFS was carried out to further understand the local atomic environment and electronic structure of the Ir/TiO₂ samples [34]. The discrepancy in oscillation between Fourier transform (FT) EXAFS spectra (Fig. S1) indicates the difference in the coordination structure of Ir species. As shown in Fig. 1f–h, combining the peaks displayed in R-space with the specific signals of elements in k and R-space provided from wavelet transform (WT) analysis can provide a more intuitive interpretation [35,36]. The maximum intensity of all the Ir/TiO₂ samples appeared around 5.3 Å⁻¹, corresponding to the Ir–O contribution. Based on the EXAFS fitting curves (Table S1), other amplitudes at the second shell were attributed to Ir–Ti contribution, with a significant difference between its bond length (ranging from 3.134 to 3.489 Å) and Ir–O–Ir bond length (3.229 and 3.594 Å). It was observed that there is no contribution of Ir–Ir or Ir–O–Ir, confirming that isolated single atomic sites are dominant for Ir loading of 0.2–0.8 wt.% in Ir/TiO₂ samples [33, 37]. As summarized in Table S1, the average coordination number (CN) of Ir–O is between 5–6, and that of Ir–Ti is between 4–6. The total CN of Ir cation is 9, 10.8, 11.3 in turn, with the increase of Ir loading. The difference in CN of Ir–O in the three samples may be due to the

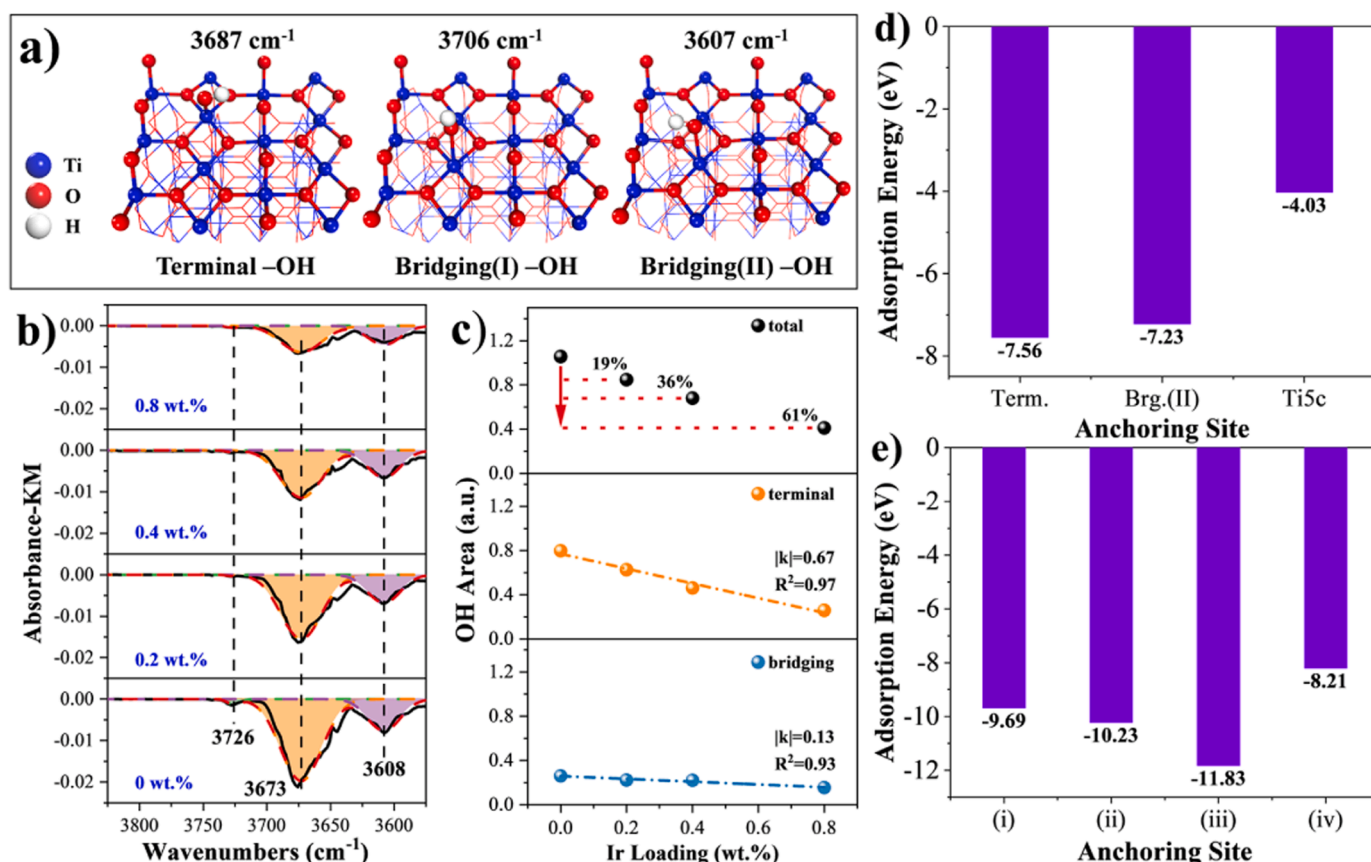


Fig. 3. DFT and in situ DRIFTS of Ir/TiO₂ samples. (a) Optimized periodic models of the hydroxylated TiO₂ (110) surface, (b) Peak resolution of -OH consumption peaks after in situ DRIFTS of NH₃ adsorption over Ir/TiO₂ with different Ir loadings (0, 0.2, 0.4 and 0.8 wt.%) at 40 °C, (c) Relationship between Ir loading and peak areas of -OH groups over Ir/TiO₂, (d) Ir adsorption energy over single site on terminal -OH (labeled term.), bridging(II) -OH (labeled brg.) and Ti_{5c}, (e) Ir adsorption energy in multiple OH complex environment, and the structures of anchoring site are as follows: (i) term.+term.+Ti_{5c} (Fig. S10), (ii) term.+term.+term. (Fig. S11), (iii) term.+term.+brg. (Fig. S12), (iv) brg.+term.+Ti_{5c} (Fig. S13).

adsorption of H₂O in the air by Ir cations to form new hydroxyl groups. It is confirmed that the structure of Ir and Ti atoms bridged by O atoms is shown in the inset.

3.2. Analysis of the anchoring sites

Three possible anchoring sites, i.e., unsaturated penta-coordinated Ti cation (Ti_{5c}), O_v, and -OH groups, have been reported on oxide surfaces (both reducible and nonreducible oxides have been referenced). Fig. 2 shows the relaxed structure of the dominant (110) surface on TiO₂ [38]. First of all, abundant Ti_{5c} sites expose on the surface. It has been widely reported that the Ti_{5c} cations provide repulsive lateral force or bridging sites for the adsorption and migration of molecules or atoms, such as CO₂, CO [39,40], and Au atom [41]. Kwak et al. proposed that the coordinative saturation of unsaturated sites is the driving force for metal atom anchoring on nonreducible oxides [25]. Therefore, as unsaturated coordinating cations, Ti_{5c} should be marked as the first type of anchoring site. In addition, the previous description mentioned that the defect sites are the direct mediators for electron transfer between the reducible oxide support and the loaded components. The atomic defects formed on the surface of TiO₂ introduce excess electrons into the surrounding lattice, leading to suitable adsorption sites such as O_v [42,43]. The distribution and dynamics of O_v can significantly affect the dispersion and shape of metal particles. For example, Au particles do not bind to a perfect TiO₂ surface, but have a binding energy of about 1.6 eV at per defect [21]. The surface O_v on defective TiO₂ nanosheets could effectively stabilize the single-atom Pt₁ by building a Ti-Pt-Ti structure [44]. Therefore, O_v is marked as the second type of anchoring site. The

last possible anchoring environment is related to the -OH groups, which is affected by the preparation environment. Wang et al. revealed that Al³⁺_{penta} sites could be easily coordinatively saturated through the interaction with H₂O, and the single-atom Ag₁ is anchored by the terminal Al-OH group through oxygen bridges [27]. There are enough water molecules in the air to hydroxyl on the oxide surface, providing a third site for Ir anchoring.

The existence of O_v over samples was further verified by electron paramagnetic resonance (EPR) experiments. TiO₂ sample exhibits a pair of steep peaks with a symmetric distribution (Fig. S2) in accordance with a signal at g = 2.008, an indication of electron trapping at O_v [45]. In contrast, no O_v signal is observed on all the Ir/TiO₂ samples, unambiguously proving that the contribution of O_v to Ir anchoring is limited. The O 1 s XPS spectra were used to quantitatively compare the amount of O_v. The peaks at 531.38 eV, 530.88 eV and 529.77 eV belong to surface-adsorbed oxygen species (labeled O_{surf}), surface O_v for TiO₂, and lattice oxygen in TiO₂ (labeled O_{latt}), respectively [46–49]. The percentage of O_v in surface O species for TiO₂ sample is calculated to be 2.90% (Table S2), since rutile phase is thermodynamically stable with weak electron-hole separation ability [46,50]. While the percentage of O_{surf} decreased from 14.97% to 8.51% as the Ir loading increases. O_{surf} species include adsorbed molecular water, and -OH, etc., where -OH groups are usually dominant [51,52].

Two types of OH groups could be identified in TiO₂, i.e., terminal -OH group and bridging -OH group, as shown in Fig. S3. According to previous reports, each oxygen atom is surrounded by two Ti atoms and one H atom at the center of a triangle. Since the sides of the triangle have different lengths, there may be two types of the bridging -OH group

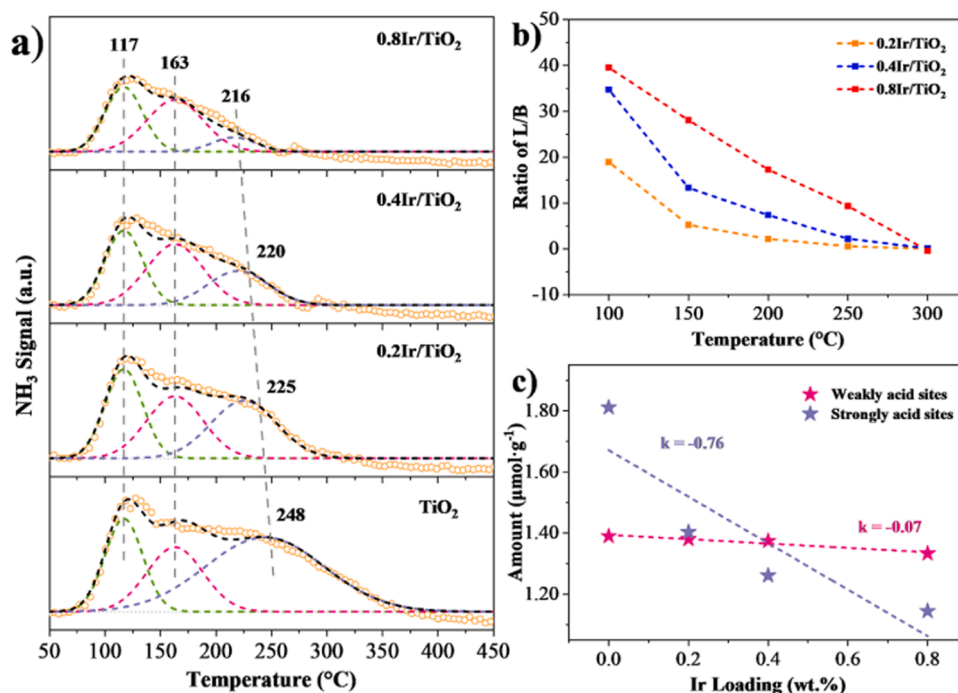


Fig. 4. The chemical properties of Ir/TiO₂ samples with different Ir loadings (0, 0.2, 0.4 and 0.8 wt.%). (a) TPD profiles of NH₃, (b) Changes in the relative amount of Lewis acid sites and Brønsted acid sites (L/B) with temperature according to in situ DRIFTS, (c) Amount of acid sites according to NH₃-TPD.

(labeled bridging(I) –OH and bridging(II) –OH, respectively) [53]. Optimized periodic models of the hydroxylated TiO₂ (110) surface were shown in Fig. 3a. Three O–H stretching frequencies corresponding to two types of –OH groups were calculated [54], wherein, 3687 cm^{−1} can be assigned to terminal –OH, while 3706 cm^{−1} and 3607 cm^{−1} can be assigned to bridging –OH. The type and relative percentage of –OH groups can be detected by in situ DRIFTS analysis using NH₃ as a probe [55,56]. Once Ir atoms occupy some of the –OH groups on TiO₂, the intensities of negative OH peaks would decrease since fewer OH sites are available for NH₃ adsorption [27]. The calculation results of stretching frequency are used to guide the attribution of OH bands in the spectra (Fig. 3b). The negative bands at 3726 cm^{−1}, 3673 cm^{−1} and 3608 cm^{−1} are assigned to the occupation of isolated –OH group of bridging(I) –OH, terminal –OH and bridging(II) –OH [53,57].

As shown in Fig. 3c, the total –OH area decreases by 19%, 36% and 61% with the increase of Ir loading (0.2, 0.4 and 0.8 wt.%), indicating that –OH sites are partially occupied by Ir species. Individual peak areas were calculated by integration and then the correlation between the Ir loading and the consumption of different types of –OH groups were analyzed. The area of terminal –OH group changes more significantly with the increase of Ir loading ($|k| = 0.67$), which is higher than the slope of the bridging –OH group ($|k| = 0.13$). The linear correlation between the area of terminal –OH group and Ir loading capacity is 0.97, which is slightly higher than that of bridging –OH group (0.93). These results strongly support the anchoring of Ir species on the TiO₂ surface through their interaction with –OH groups, particularly with terminal –OH group. Although the specific surface area of rutile TiO₂ is significantly lower than that of anatase TiO₂ (Table S3), a sufficient amount (75.4%) of terminal –OH groups actually provides more possibilities for Ir cations disperse at atomic level (Fig. S4).

The anchoring effects of the –OH groups were verified by DFT theoretical calculations, and the binding energy of Ir and Ti_{5c} site was compared. An optimized periodic model of the rutile TiO₂ (110) surface were shown in Fig. S5. The periodic models of terminal –OH, bridging –OH and Ti_{5c} site were constructed and optimized (Figs. S6–S9). In Fig. 3d, the binding energies of Ir anchored at the three single sites (terminal –OH, bridging(II) –OH and Ti_{5c} site) are negative, indicating

that all three anchoring sites have strong affinity for Ir. Furthermore, the lowest binding energy occurred at terminal –OH site (−7.56 eV). At the same time, the original Ti–O bond between the –OH group and TiO₂ support is cut off due to the intervention of Ir species. It is confirmed that Ir atom cannot directly anchor at a certain –OH group, but forms a multi-coordination structure with surrounding atoms. In contrast, the Ir species cannot be stably adsorbed on the bridging(I) –OH site. The coordination environment of terminal –OH as the center is enriched by various –OH groups, as shown in Fig. 3e, and the binding energy of Ir anchored at the terminal –OH site is further reduced. The optimized model details are shown in Figs. S10–S13. Especially when the two sides of the terminal –OH anchoring center are filled with one terminal –OH and one bridging –OH respectively, the binding energy of Ir reduces to −11.83 eV. These results confirm that Ir cations preferentially displace H⁺ in Ti–OH to disperse, and the coordination structure is also influenced by the surrounding environment. The most stable coordination structure should be grateful for the simultaneous consumption of multiple –OH groups, and the CN is close to the fitting result of XAFS.

3.3. Surface acidity and NH₃-SCO reaction mechanism

It is well known that the –OH group, as one of Brønsted acid sites, plays an important role in the NH₃-SCO reaction [13]. Therefore, we evaluated the acidities of the samples after loading Ir through NH₃-TPD analyses. The amount of physisorbed NH₃ (located at 117 $^{\circ}\text{C}$ in Fig. 4a) was affected by a decrease of specific surface area (Table S3). While the loading of Ir inhibits the chemisorption of NH₃, and the desorption peaks at 163 $^{\circ}\text{C}$ and 216–248 $^{\circ}\text{C}$ are attributed to the weakly acid sites and the strongly acid sites, respectively [58,59]. Actually, the strength of the strongly acid sites decreases with the increase of Ir loading. As shown in Fig. S14 and Fig. 4b, although mutual conversion would occur between ionic NH₄⁺ adsorbed on the Brønsted acid sites (B–NH₄⁺ at 1436 cm^{−1}) and NH₃ coordinated to the Lewis acid sites (L–NH₃ at 1178 cm^{−1}) in the low temperature range (150–250 $^{\circ}\text{C}$), the B–NH₄⁺ is more stable than the L–NH₃ since it has not fully desorbed at 300 $^{\circ}\text{C}$. The relative content of Lewis acid sites decreases with increasing temperature for all Ir/TiO₂ samples. Therefore, the strongly acid sites are mainly served by the

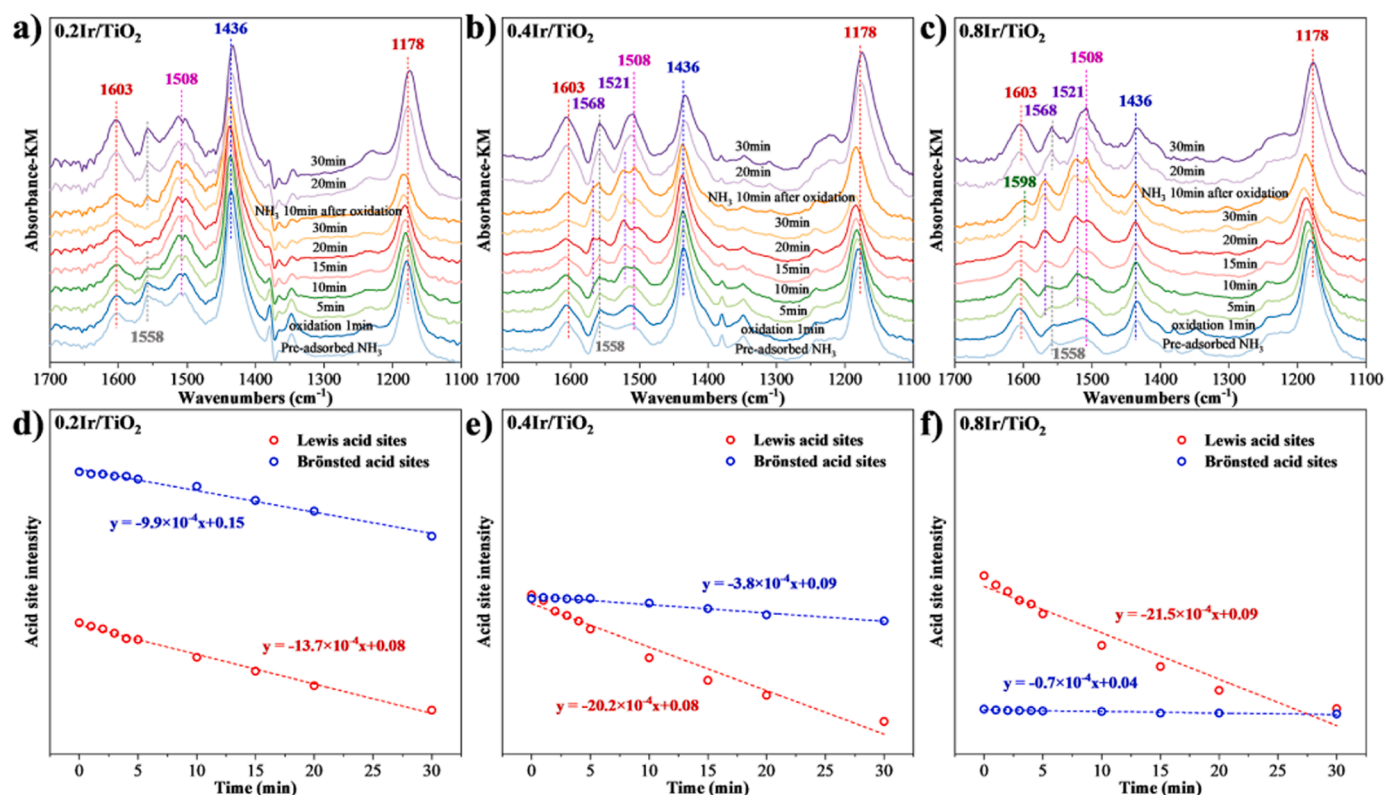


Fig. 5. In situ DRIFTS results for the reaction between O₂ and pre-adsorbed NH₃ species over (a) 0.2Ir/TiO₂, (b) 0.4Ir/TiO₂, (c) 0.8Ir/TiO₂. And the consumption rate of Lewis and Brønsted acid sites under O₂ on (d) 0.2Ir/TiO₂, (e) 0.4Ir/TiO₂, (f) 0.8Ir/TiO₂. Reaction conditions: 400 ppm NH₃, 10% O₂ in N₂ at 200 °C.

Brønsted acid sites. We believe that the loading of Ir cation acts as electron donating groups, reducing the degree of charge delocalization on the neighboring oxygen atom compensated by the proton [60]. Moreover, the amount of acid sites could be quantified by deconvolution. In Fig. 4c, the slope is used to reflect the degree of decrease in the number of acid sites, which reaches -0.76 in strongly acid sites and is only -0.07 in weakly acid sites. The decrease in the amount of strongly acid sites is due to Ir cation occupying some of the $-OH$ groups, but new Lewis acid sites are formed at the electron-deficient area as the intensity of EMSI between support and Ir cation gradually increased [61].

The reaction mechanism of NH₃-SCO on Ir/TiO₂ catalysts was investigated at 200 °C by using in situ DRIFTS. Dynamic spectra of injecting O₂ onto pre-adsorbed NH₃ samples are presented in Fig. 5a–c. According to previous studies, the bands at 1603, 1178 cm⁻¹ were ascribed to NH₃ coordinated to the Lewis acid sites (L-NH₃), the bands at 1436 cm⁻¹ was related to ionic NH₄⁺ adsorbed on the Brønsted acid sites (B-NH₄⁺), the bands at 1558 cm⁻¹ and 1508 cm⁻¹ were due to $-NH_2$ species and monodentate nitrate, respectively [62–65]. It confirms that the role of O_{latt} in dehydrogenation and oxidation to form monodentate nitrate cannot be ignored. For 0.2Ir/TiO₂ sample, the peaks of L-NH₃, B-NH₄⁺ and $-NH_2$ species slowly decreased with the injection of O₂, while the peak of monodentate nitrate become more pronounced. When the injection of O₂ was cut off and the sample was exposed to NH₃ again, the peak of these adsorbed species almost returned to the initial level. This indicates that nitrate species are key intermediates after the dehydrogenation of adsorbed NH₃ and can be reduced by subsequent gas-phase NH₃, following the internal selective catalytic reduction (i-SCR) mechanism, and is usually responsible for high N₂ selectivity [8, 66–68]. The bidentate and bridging nitrates were also observed at the same temperature on 0.4Ir/TiO₂ and 0.8Ir/TiO₂ samples. Among them, the peaks of bidentate nitrate (1568 and 1521 cm⁻¹) appeared 10 min after O₂ injection on 0.4Ir/TiO₂ but appeared 5 min after O₂ injection on 0.8Ir/TiO₂. While the peak of bridging nitrate (1598 cm⁻¹) were

observed at 30 min only on 0.8Ir/TiO₂ [69,70].

The peak consumption rate of Lewis and Brønsted acid sites during the injection of O₂ were fitted in Fig. 5d–f. The initial acid site intensity was determined by the amount of acid sites on the Ir/TiO₂ samples, and L-NH₃ gradually dominated with the increase of Ir loading compared to B-NH₄⁺. And the consumption rate of L-NH₃ was always higher than that of B-NH₄⁺. On the 0.2Ir/TiO₂ sample, the consumption rate of L-NH₃ was about -13.7×10^{-4} , only slightly higher than the consumption rate of B-NH₄⁺ (-9.9×10^{-4}). However, the difference between them gradually increased as L-NH₃ dominated. On the 0.4Ir/TiO₂ sample, the consumption rate of L-NH₃ increased to -20.2×10^{-4} , while the consumption rate of B-NH₄⁺ decreased to -3.8×10^{-4} . While the consumption rate of B-NH₄⁺ was close to zero, and the active species were almost entirely L-NH₃ ones on 0.8Ir/TiO₂ sample. These results indicate that both L-NH₃ and B-NH₄⁺ can convert to nitrates under the reaction of O₂, and the dehydrogenation rate of L-NH₃ is higher than that of B-NH₄⁺, making it easier to support the generation of bidentate and bridging nitrates at low temperatures.

3.4. Electron effect and NH₃-SCO performance

As previously reported [37,71–73], the energy position of the white line is highly sensitive to metals valence states, due to it is proportional to the d-orbital density of states. For Ir/TiO₂ samples, their white line intensity was significantly higher than that of Ir foil, suggesting that Ir species carry positive charges (Fig. S1). Interestingly, the higher integrated white line intensity appeared with increasing Ir load increases indicates the emptier d-orbital states (d holes) and higher oxidation states of 0.8Ir/TiO₂ than 0.4Ir/TiO₂ or 0.2Ir/TiO₂, which may lead to enhanced EMSI [61,74,75]. This is supported by the fitting results of Ir–O bonding distance in Table S1, which are close to the IrO₂ standard sample. The electronic perturbations caused by EMSI can be described as the change of the d-band center relative to the Fermi level [75,76]. An

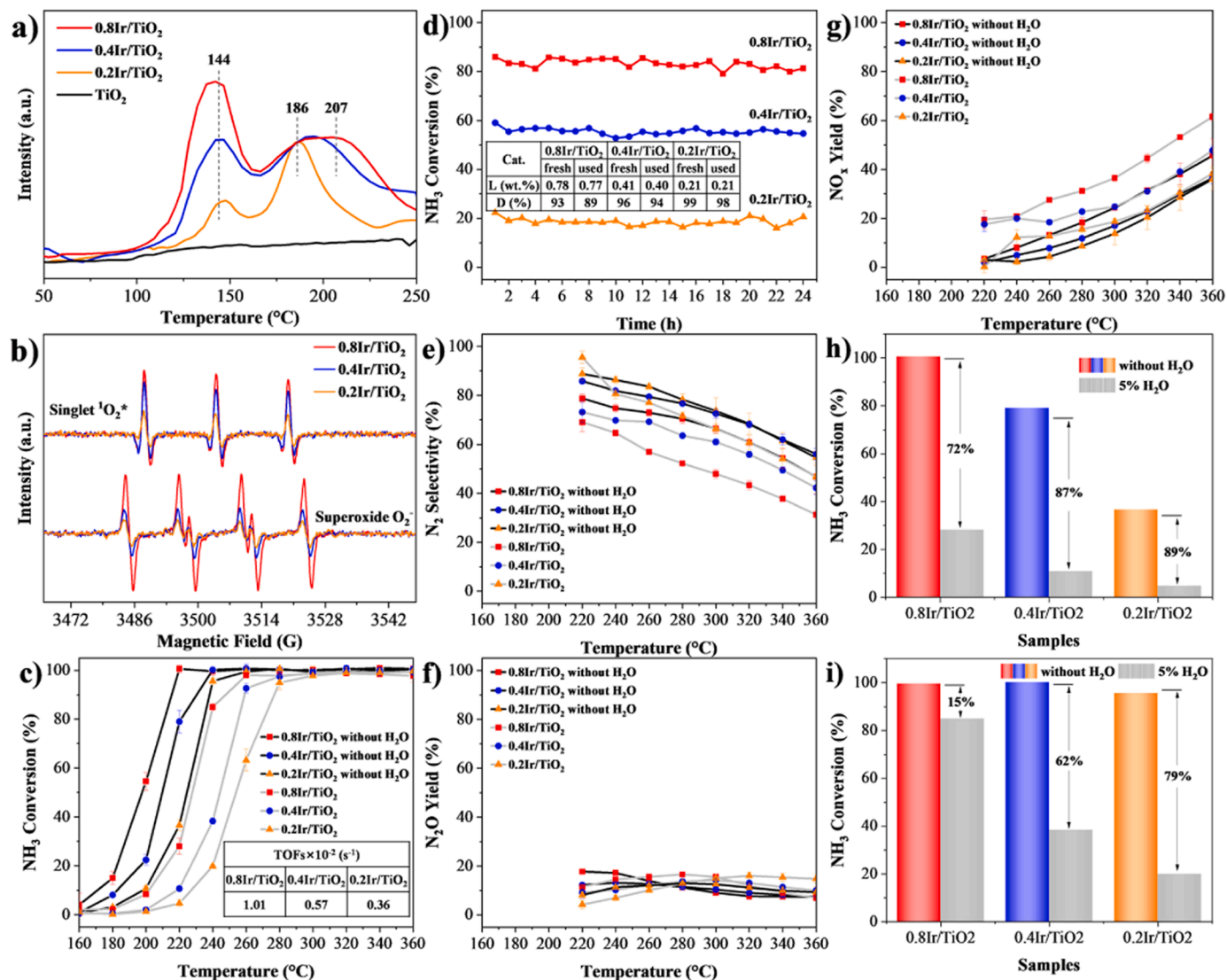


Fig. 6. Electron effect and NH_3 -SCO performance of Ir/TiO_2 catalysts with different Ir loadings (0.2, 0.4 and 0.8 wt.%). (a) TPR profiles of H_2 , (b) EPR signals of singlet $^1\text{O}_2^*$ (upper) with 2,2,6,6-tetramethyl-4-piperidone (TEMP) and superoxide O_2^- (down) with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) spin trapping agent, (c) NH_3 conversion, (d) 24 h stability tests at 210°C , together with Ir loading (L) and Ir dispersion (D) for fresh and used samples. (e) N_2 selectivity, (f) N_2O yield, (g) NO_x yield. Reaction conditions: 400 ppm NH_3 , 10% O_2 and 5% H_2O (when used) in N_2 , GHSV = $85\,000\text{ h}^{-1}$. TOFs were obtained at 200°C , and the reaction conditions were as below: 400 ppm NH_3 and 10% O_2 in N_2 , GHSV = $85\,000$ – $340\,000\text{ h}^{-1}$. (h) Contrast of NH_3 conversion in dry and wet circumstances at 220°C , (i) Contrast of NH_3 conversion in dry and wet circumstances at 240°C .

ideal upshift would improve chemical and catalytic properties, which are usually more conducive to O_2 activation by depleting the outer orbitals electrons and increasing the density of states (DOS) of the anti-bonding π^* orbital. The H_2 -TPR experiment was used to study the redox properties of the samples, as shown in Fig. 6a. The reduction peak of adjacent TiO_2 oxides under the action of EMSI occurred at 186 – 207°C [24]. Since the increase of the total CN of Ir cation will lead to the expansion of the difference in each bond length and bond energy, the reduction peak band shows a gradual broadening. The peak at 144°C belongs to the reduction of adsorption activated O_2 at the interface of single-atom Ir_1 and the support, which changed with the number of interface sites. The reduction peak of oxygen species on the TiO_2 support cannot be observed within the temperature range of 50°C – 250°C . This is because as a stable crystalline structure, it is difficult to form oxygen defects on the surface of rutile. In Fig. 6b, EPR spectra of all the Ir/TiO_2 samples with TEMP and DMPO spin trapping agent displayed 1: 1: 1 triplet and 1: 1: 1 quartet split signal, denoting the adsorption activated O_2 exists as singlet $^1\text{O}_2^*$ and superoxide O_2^- species, respectively

[77,78].

The NH_3 -SCO performance of Ir/TiO_2 catalysts were evaluated in dry and wet circumstances. In Fig. 6c, NH_3 conversion (dry circumstance) over the $0.2\text{Ir}/\text{TiO}_2$ catalyst started at 200°C and reached 36% at 220°C . As the Ir loading increases to 0.4 wt.% and 0.8 wt.%, the NH_3 conversion was 79% and even 100% at 220°C , respectively. It can be seen that although a single-atom Ir_1 is an active site, TOF is not constant. The TOF of $0.8\text{Ir}/\text{TiO}_2$, $0.4\text{Ir}/\text{TiO}_2$ and $0.2\text{Ir}/\text{TiO}_2$ catalysts was $1.01 \times 10^{-2}\text{ s}^{-1}$, $0.57 \times 10^{-2}\text{ s}^{-1}$ and $0.36 \times 10^{-2}\text{ s}^{-1}$, respectively. The dehydrogenation of adsorbed NH_3 under the reaction of active oxygen species is the rate-determining step in the NH_3 -SCO reaction, which is influenced by both the NH_3 adsorption strength and oxygen activation ability. Among them, the active site is responsible for providing reactive oxygen species, while NH_3 adsorption strength is dominated by acid sites. Therefore, TOF would be affected by both active and acid sites, and the faster dehydrogenation rate of L-NH_3 promotes the reaction rate of NH_3 at the same active site. Tests conducted for 24 h revealed that the Ir/TiO_2 samples has excellent stability, and NH_3 conversion remained at

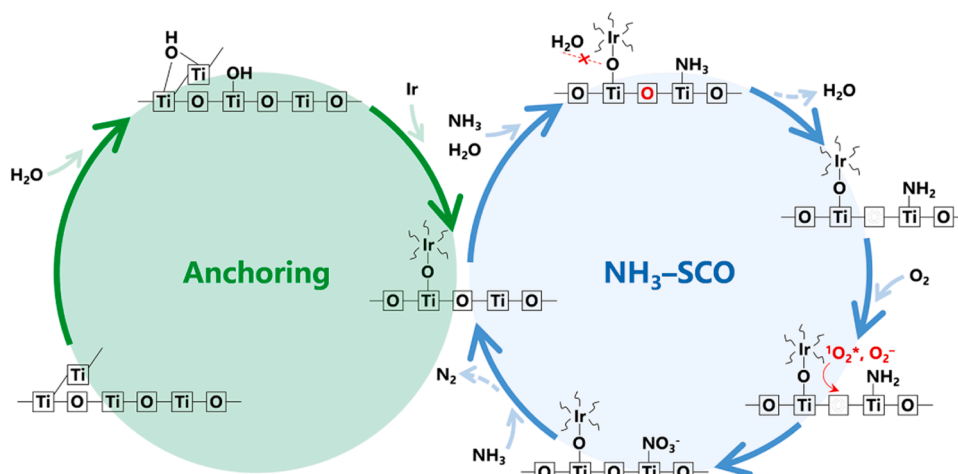


Fig. 7. Anchoring mechanism of active species on TiO_2 and the NH_3 -SCO reaction mechanism over Ir/TiO_2 catalyst.

83%, 55%, and 19% at 210 °C on three samples. As well as there was almost no change in the aggregation and loading of active components under the reaction conditions, as shown in Fig. 6d. This indicates that the anchoring of Ir on the TiO_2 surface is relatively stable. Meanwhile, the N_2 selectivity was higher than 78% at 220 °C (Fig. 6e), and gradually decreased with increasing temperature. Within the experimental temperature range of 160 °C–360 °C, NO_x is the main by-product compared to N_2O . Especially in the temperature range of 220 °C to 360 °C, the conversion of NH_3 to NO_x was significantly promoted, while the yield of N_2O remained below 20% (Fig. 6f–g). It is indicated that the peroxidation ability of catalysts is promoted at high temperatures, generating more unexpected by-products. We also found that a lower surface Ir loading on the catalyst is more favorable for the selective generation of N_2 , which should be responsible by the corresponding relationship between O_2 activation ability and Ir loading, as demonstrated by the H_2 -TPR experiment. Although the rate-determining step is controlled by the difficulty of O_2 activation, there should be an equilibrium between them. Once the nitrate species generate too fast and directly desorb without a secondary reaction with subsequent gas-phase NH_3 , the generation of NO_x can be foreseen. Therefore, the appropriate O_2 activation ability on the catalyst is crucial for improving N_2 selectivity.

We further examined the NH_3 -SCO performance of Ir/TiO_2 catalysts in wet circumstance, and compared our results with previously reported catalytic systems (Fig. 6h–i and Table S4). On 0.2Ir/ TiO_2 sample, 89% NH_3 conversion dropped with the addition of 5% H_2O at 220 °C, while the descent rate was 87% or 72% for 0.4Ir/ TiO_2 and 0.8Ir/ TiO_2 samples. This indicates that water resistance is related to the amount of Ir loading. The superiority of 0.8Ir/ TiO_2 sample in wet circumstance becomes more apparent at 240 °C, with the descent rate of NH_3 conversion only decreasing by 15%, while the decrease rates of other samples are still above 60%. Our previous research has shown that the negative effect of water is due to the competitive adsorption of water molecules with NH_3 [14]. According to other studies, water molecules are attracted and adsorbed on the surface of the material by forming hydrogen bondings with -OH groups [79]. We believe that the anchoring of Ir occupies and consumes the surface -OH groups of TiO_2 , thereby reducing the competitive adsorption of water vapor, which is the main reason for the excellent water resistance in 0.8Ir/ TiO_2 . This result is extremely similar to the water resistance of Ag based zeolites in wet conditions, as Al-OH is an important anchoring site for Ag cation [27,80]. It should be noted that the injection of water vapor also leads to a further increase in the yield of NO_x , resulting in lower N_2 selectivity, particularly evident on the 0.8Ir/ TiO_2 sample (presented in Fig. 6e and g). We speculate that although the lack of -OH groups reduce the competitive adsorption between H_2O and NH_3 molecules, water vapor is likely to directly participate in the intermediate conversion process in gaseous form,

promoting the generation of nitrate species.

4. Discussion

This work demonstrates that the -OH groups are the key sites for metal-support interactions that affect the morphology and dispersion of Ir species on TiO_2 , and the activity and water resistance of the loaded Ir/ TiO_2 samples in the NH_3 -SCO reaction. Based on measurements by HAADF-STEM, XAFS, EPR, XPS, in situ DRIFTS and DFT, we reveal that the Ir species anchor at the terminal -OH groups on TiO_2 mainly through oxygen bridges. The source of the oxygen bridge is the coordinative saturation of the Ti_{5c} site through the interaction with H_2O . DFT calculations confirm that the binding energy of Ir in a multiple hydroxyl environment is as low as -11.83 eV, but still with the terminal -OH as anchoring center. The fitting results between the optimized model and XAFS confirmed that the CN of Ir-O bond was close to 5, and the Ir-Ti coordination was dominant in the second shell. This is important evidence for the atomic-level dispersion of Ir species on the TiO_2 , which caused by the amount of terminal -OH groups on the surface of rutile TiO_2 are as high as 75.4%. The consumption of -OH groups on Ir/ TiO_2 samples varies linearly with the increase of Ir loading, resulting in the more active coordinated L- NH_3 gradually becoming dominant.

The adsorption strength of NH_3 is another key factor affecting the reaction rate-determining step, namely NH_3 dehydrogenation, which has a significant contribution to improving the low-temperature activity of NH_3 -SCO. On the one hand, the dehydrogenation rate of L- NH_3 is higher than that of B- NH_4^+ , which significantly increases the reaction rate of NH_3 at a single active site by promoting the low-temperature formation of bidentate and bridging nitrates. The active oxygen species involved in this process include O_{latt} and singlet $^1\text{O}_2^*$ or superoxide O_2^- species at the interface, under the reaction of EMSI between support and Ir cation. Afterwards, the reaction follows the i-SCR mechanism, and all nitrate intermediates are reduced by subsequent NH_3 , achieving high N_2 selectivity. The relevant reaction process is illustrated in Fig. 7. On the other hand, the coordinated L- NH_3 significantly avoids the competitive adsorption of water vapor in the NH_3 -SCO reaction by reducing the number of hydrogen bonding. Since the strong ability of the catalysts to adsorb water is attributed to the formation of hydrogen bondings through -OH groups, and the amount of -OH groups on the TiO_2 surface is balanced by loading highly dispersed Ir species.

5. Conclusions

In summary, this work has studied that the -OH groups, as an important anchoring site for the dispersion and stability of Ir species on TiO_2 , plays a decisive role in the reaction rate-determining step, namely

NH₃ dehydrogenation in NH₃-SCO reactions. The 0.8Ir/TiO₂ sample shows higher reaction rate of NH₃ at a single active site and lower competitive adsorption of water vapor than 0.2Ir/TiO₂ and 0.4Ir/TiO₂, attributed to the highest L-NH₃ ratio. Finally, the NH₃ conversion is 85% in a wet circumstance (5% H₂O) at 240 °C (GHSV = 85 000 h⁻¹), with a N₂ selectivity of up to 65% on 0.8Ir/TiO₂ sample. These results suggest that the adsorption strength of NH₃ is another influencing factor that besides O₂ activation and plays an important role in the NH₃-SCO reaction rate-determining step. On the other hand, it further guides the synthesis of high-utilization metals on vacancy-deficient reducible oxides.

CRediT authorship contribution statement

Xu Wenqing: Project administration, Resources, Writing – review & editing, Software. **Wang Yixi:** Validation, Visualization, Writing – original draft. **He Hong:** Writing – review & editing. **Yang Jun:** Writing – review & editing. **Yang Yang:** Writing – review & editing, Formal analysis. **Ma Jinzhu:** Software, Writing – review & editing. **Li Chaoqun:** Formal analysis, Methodology. **Zhu Tingyu:** Project administration, Resources, Supervision, Software.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123684](https://doi.org/10.1016/j.apcatb.2023.123684).

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